Synthesis of Hydride Tantalabenzocyclopentene and μ-Alkylidene Complexes by Direct Alkylation Reactions of [TaCp*Cp′Cl$_2$] − NMR Spectroscopic Study and X-ray Crystal Structure of [TaCp*Cp′(H)(η^2-CH$_2$-CMe$_2$-*o*-C$_6$H$_4$)], (Cp* = η^5-C$_5$Me$_5$; Cp′ = η^5-C$_5$H$_4$SiMe$_3$)

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The reaction of [TaCp*Cp′Cl$_2$] with 1 equiv. of [Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$] or 2 equiv. of LiCH$_2$R (R = SiMe$_3$, CMe$_3$) leads to the formation of bis(μ-alkylidene) complexes [(TaCp*Cp′)$_2$(μ-CHR)$_2$], (R = C$_6$H$_5$, **1**; SiMe$_3$, **2**; CMe$_3$, **3**), whereas the alkylation of [TaCp*Cp′Cl$_2$] with 2 equiv. of LiCH$_2$CMe$_2$Ph gives the hydride tantalabenzocyclopentene complex [TaCp*Cp′(H)(η^2-CH$_2$–CMe$_2$-*o*-C$_6$H$_4$)] (**4**). All the complexes were characterized by IR and NMR spectroscopy. The molecular structure of complex **4** has been determined by X-ray diffraction methods. Complex **4** crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions of a = 8.976(1) Å, b = 16.596(1) Å, c = 17.929(1) Å, β = 99.26(1)°, V = 2636(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.478 g·cm^{-3}, $R1$ = 0.0481 and $wR2$ = 0.133.

Introduction

Early transition metal alkylidene complexes are versatile organometallic compounds due to their participation as intermediates in a number of important stoichiometric and catalytic processes.[1] Likewise, the importance of such complexes is quite clear in the studies of olefin metathesis reactions[2] having shown to catalyze the polymerization of strained ring systems in ring opening metathesis polymerization (ROMP) and polymerization of acyclic dienes (ADMET).[1d,11,4] μ-Alkylidene complexes with the ligand bridging two metal centers have been investigated in more recent times and postulated as intermediates in Fischer−Tropsch, olefin metathesis and Ziegler−Natta catalysis processes.[1] Alkylidene compounds can be made, among other methods,[1] by an α-H abstraction from transition metal alkyls[5] in an intramolecular or intermolecular process, as has been demonstrated both for early[5] and late[6] transition metal complexes.

Transition metal metallacycles are the subject of considerable current interest[7,8] and sufficient evidence has been gained to demonstrate conclusively their participation in a number of catalytic reactions such as alkene metathesis[9] and oligomerizations,[10] C−H bond activation[11] and hydrocarbon isomerization.[12] Metallacyclic complexes have been obtained by intramolecular activation of a distal C−H bond of a coordinated ligand,[8e,8k,8o,13] although harder conditions are required for their activation by γ-[8a,8f,14] or δ-[4g,15]hydrogen abstraction. If the coordinated ligand is an alkyl group with distal aromatic C−H bonds, a metallacyclic compound containing both a M−C(alkyl) and a M−C(aryl) bond may be formed.[4g,8e,8k,13b,13c,16]

We report herein the results obtained in the study of the reactivity of the mixed-ring dicyclopentadienyltantalum complex [TaCp*Cp′Cl$_2$] (Cp* = η^5-C$_5$Me$_5$; Cp′ = η^5-C$_5$H$_4$SiMe$_3$) towards alkylating reagents and an NMR spectroscopy study and the X-ray molecular structure of the complex [TaCp*Cp′(H)(η^2-CH$_2$-CMe$_2$-*o*-C$_6$H$_4$)].

Results and Discussion

Toluene solutions of [TaCp*Cp′Cl$_2$] react with 1 equiv. of [Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$] or 2 equiv. of LiCH$_2$R (R = SiMe$_3$, CMe$_3$, CMe$_2$Ph) under ambient conditions to give the bis-μ-alkylidene complex [(TaCp*Cp′)$_2$(μ-CHR)$_2$], (R = C$_6$H$_5$, **1**; SiMe$_3$, **2**; CMe$_3$, **3**) and the hydride tantalabenzocyclopent-2-ene [TaCp*Cp′(H)(η^2-CH$_2$-CMe$_2$-*o*-C$_6$H$_4$)] (**4**), with simultaneous elimination of R−CH$_3$ (R = C$_6$H$_5$, SiMe$_3$, CMe$_3$) and PhMe$_2$C−CH$_2$−CH$_2$−CMe$_2$Ph, respectively (Scheme 1). All of the eliminated organic products were identified by ^{1}H NMR spectroscopy when the re-

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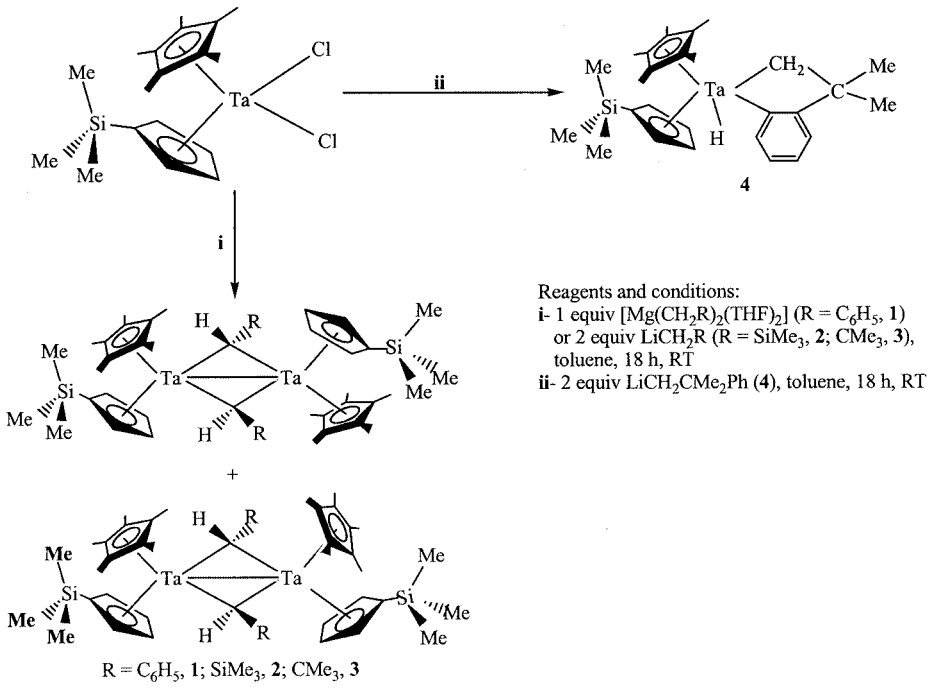


Scheme 1

actions were carried out in a sealed NMR tube with [D_6]benzene as solvent.

As a plausible reaction pathway we suggest the formation of the intermediate paramagnetic dialkyl complexes **I1**−**I4** in the first step (Scheme 2). These compounds can then evolve differently depending on the nature of the substituents: the intermediates **I1**−**I3**, undergo an α-H abstraction process[1d,1i,4g,5,7j,9d,17,18] to generate a transient tantalum(IV) alkylidene complex (step **i**), which then rearranges to form the bis-μ-alkylidene complexes **1**−**3**. It should be noted, however, that there are several examples where dialkyl [MCp_2R_2] complexes (M = Nb, Cp = η^5-C_5H_5, R = Me;[19a,19b] M = Ta, Cp = η^5-C_5H_4Me, R = Me;[19b] M = Nb, Ta, Cp = η^5-C_5H_5, R = CH_2SiMe_3;[19c] M = Ta, Cp = η^5-C_5H_5, R = Me[19d]) are thermally stable towards loss of alkane and undergo an α-elimination process.

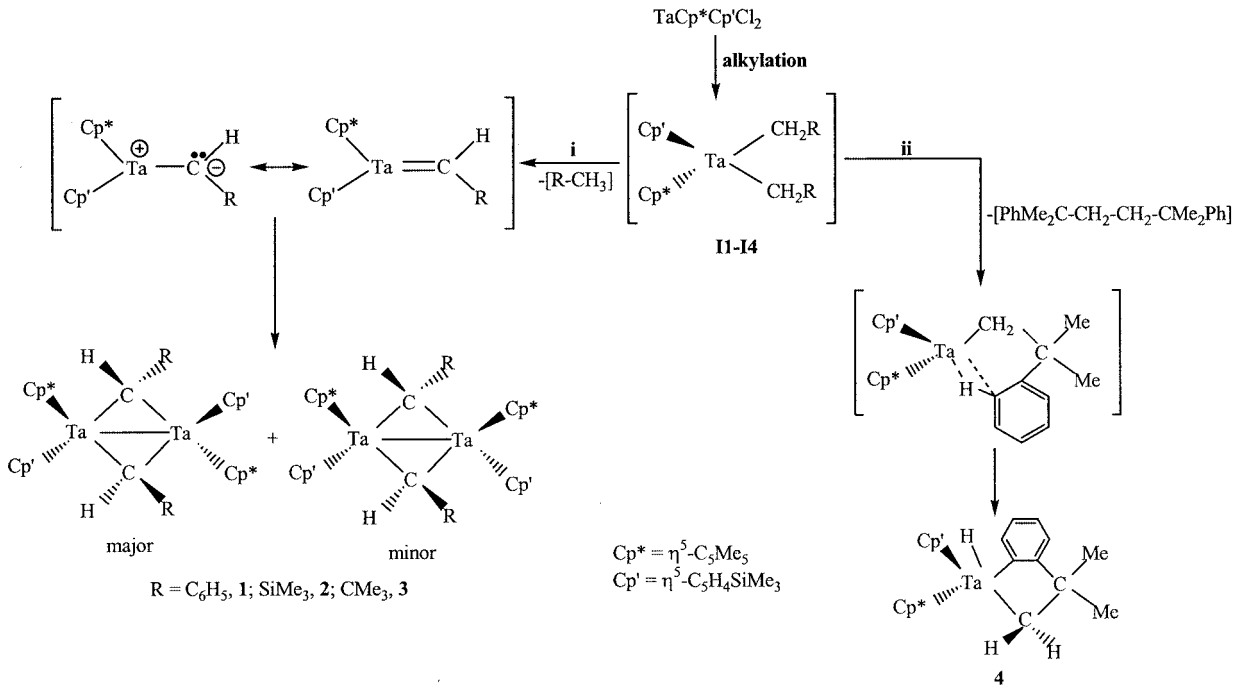
The presence of the neophyl group in the intermediate complex **I4** leads to a different reactivity with respect to that of the intermediates **I1**−**I3**. Thus, the reduction of two **I4** molecules produces the organic elimination product 2,5-dimethyl-2,5-diphenylhexane,[20] detected when the reaction is followed by ^{1}H NMR spectroscopy, and the corresponding neophyl tantalum(III) derivative (see Scheme 2, **ii**). Subsequent orthometalation of the phenyl ring produces the hydride tantalabenzocyclopent-2-ene complex **4** through the oxidative addition of a δ_{C-H} bond[8a,8e,8f,8k,8o,13−15] to the metal center.

All the complexes are soluble in aromatic and saturated hydrocarbons, diethyl ether and tetrahydrofuran. They are air- and moisture-sensitive, and rigorously dried solvents and handling under a dry inert atmosphere were found to be imperative for successful preparations. The compounds decompose rapidly upon exposure to air, both as solids and in solution.

The spectroscopic data (see Exp. Sect.) are in agreement with the proposed structures. The IR spectra show the characteristic absorptions for both cyclopentadienyl rings (Cp* = C_5Me_5:[21,22] ν_{C-C} =1030 cm^{-1}; $C_5H_4SiMe_3$:[23] ν_{C-H} = 839 cm^{-1}), as well as other internal vibrations of the different substituents [$\nu_{\delta s}(CH_3)$[24] = 1243 cm^{-1}]. The ν_{Ta-H} stretching vibration in the complex **4** appears as a broad band at 1804 cm^{-1}, in agreement with the data reported for other hydride complexes.[25]

The NMR spectroscopic data of **1**−**3** indicate the presence of two isomers for each complex in different ratios, depending on the steric bulk of the substituents [R = C_6H_5 (**1**) 9:1], (R = $SiMe_3$ (**2**) 2:1] and [R = CMe_3 (**3**) approx. 6:1] (see Exp. Sect). The trimethylsilylcyclopentadienyl ring appears as an ABCD spin system in the ^{1}H NMR spectra and five carbon resonances in the $^{13}C\{^1H\}$ NMR spectra. This pattern can be explained by the *anti*-disposition of the R (or H) group in the μ-CHR moiety with respect to the central core, which has two chiral tantalum atoms, as shown in Scheme 1, since a *syn*-disposition should show an AA′BB′ spin system in the ^{1}H NMR and three signals in the $^{13}C\{^1H\}$ NMR spectrum. We propose that the formation of two isomeric structures for **1**−**3** is related to the mutual disposition of the two different cyclopentadienyl rings: the more populated isomers are those with an *anti*-disposition of the bulkier η^5-C_5Me_5 groups.

Formulation of **4** as a hydride tantalabenzocyclopent-2-ene complex has been confirmed by a single-crystal X-ray diffraction study. The molecular structure of compound **4** is shown in Figure 1 and selected bond lengths and angles are given in Table 1. The molecule has the typical bent-



Scheme 2

metallocene structure with the tantalum atom bonded to two different cyclopentadienyl rings, and with a metallacycle system and a hydride atom located in the equatorial positions.

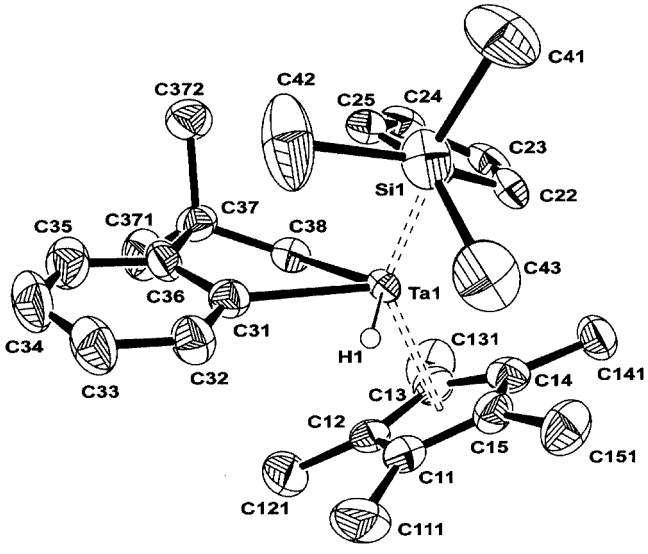


Figure 1. ORTEP view of the molecular structure of complex **4** with ellipsoids drawn at a 50% level

If Cp* and Cp′ are the centroids of the C_5Me_5 and the $C_5H_4SiMe_3$ rings, respectively, the angle Cp*−Ta−Cp′ is 133.96° and that between the planes of both cyclopentadienyl rings is 133.5°, implying that the η^5 coordination is maintained in both cases. These data are confirmed by the small range of C(Cp)−Ta distances [2.436(8) to

Table 1. Selected bond lengths (Å) and angles (°) for **4** [Cp* and Cp′ are the centroids of the C_5Me_5 and $C_5H_4(SiMe_3)$ rings, respectively]

Ta(1)−C(38)	2.306(8)	C(13)−C(131)	1.518(12)
Ta(1)−C(31)	2.309(8)	C(14)−C(15)	1.393(11)
Ta(1)−C(25)	2.406(8)	C(14)−C(141)	1.536(12)
Ta(1)−C(22)	2.406(8)	C(15)−C(151)	1.514(12)
Ta(1)−C(23)	2.414(8)	C(21)−C(25)	1.387(11)
Ta(1)−C(13)	2.440(8)	C(21)−C(22)	1.426(11)
Ta(1)−C(15)	2.437(8)	C(22)−C(23)	1.384(12)
Ta(1)−C(21)	2.438(8)	C(23)−C(24)	1.397(13)
Ta(1)−C(24)	2.450(8)	C(24)−C(25)	1.389(11)
Ta(1)−C(12)	2.457(8)	C(31)−C(36)	1.397(12)
Ta(1)−C(11)	2.464(8)	C(31)−C(32)	1.403(11)
Ta(1)−C(14)	2.466(8)	C(32)−C(33)	1.391(13)
Si(1)−C(43)	1.838(14)	C(33)−C(34)	1.385(15)
Si(1)−C(42)	1.860(11)	C(34)−C(35)	1.363(15)
Si(1)−C(41)	1.885(11)	C(35)−C(36)	1.423(12)
Si(1)−C(21)	1.884(8)	C(36)−C(37)	1.505(12)
C(11)−C(12)	1.387(13)	C(37)−C(38)	1.522(12)
C(11)−C(15)	1.408(12)	C(37)−C(371)	1.546(12)
C(11)−C(111)	1.506(12)	C(37)−C(372)	1.560(12)
C(12)−C(13)	1.428(12)	Cp*−Ta(1)	2.143
C(12)−C(121)	1.521(12)	Cp′−Ta(1)	2.112
C(13)−C(14)	1.398(12)		

C(38)−Ta(1)−C(31)	69.3(3)	C(31)−C(36)−C(37)	118.9(7)
C(43)−Si(1)−C(42)	111.4(7)	C(35)−C(36)−C(37)	121.2(8)
C(43)−Si(1)−C(41)	109.9(7)	C(36)−C(37)−C(38)	105.8(7)
C(42)−Si(1)−C(41)	108.7(7)	C(37)−C(38)−Ta(1)	119.8(5)
C(43)−Si(1)−C(21)	111.8(5)	Cp*−Ta(1)−Cp′	133.96
C(42)−Si(1)−C(21)	110.0(5)	C(38)−Ta(1)−Cp′	103.26
C(41)−Si(1)−C(21)	104.8(5)	C(38)−Ta(1)−Cp*	102.47
C(36)−C(31)−C(32)	116.2(8)	C(31)−Ta(1)−Cp′	111.30
C(36)−C(31)−Ta(1)	119.5(6)	C(31)−Ta(1)−Cp*	113.30
C(32)−C(31)−Ta(1)	124.3(7)		

2.466(8) Å for the Cp* ring and 2.406(8) to 2.449(8) Å for the Cp′ ring]. The Ta−Cp(centroid) distances are 2.143 Å for Cp* and 2.112 Å for Cp′. It is interesting to note that the value of the Cp*−Ta−Cp′ angle (133.96°) is smaller than that found in [TaCp*Cp′′H_3][21] (142.6°) or in [TaCp*$_2H_3$][23b] (148.3°), probably due to the bigger size of the equatorial ligand and the smaller size of the Cp′ ligand with respect to Cp′′, and it is even smaller than the angle found in *ansa*-bridged tantalum(III) hydride complexes such as [Ta{$Me_2Si(C_5Me_4)_2$}H(CO)][26] where the value is 139.7°.

The metallacycle moiety is located in the equatorial positions. If we define the equatorial plane with the Ta, C31 and C38 atoms, the distances to this plane of Cp*(1.96 Å) and Cp′(1.95 Å) are essentially the same, and the phenyl ring plane makes an angle of only 13.9(2)° with it. If we consider the Cp*−Ta−Cp′ plane, the metallacycle is located unsymmetrically with respect to it. The distances of C31, C36, C37 and C38 to this plane are 0.558, −0.418, −1.895 and −1.839 Å, respectively, with the more sterically demanding moiety of the ligand located in a lateral position leaving space for the hydride on the other side, near to the phenyl ring, as we can be seen in Figure 2. Compound **4** is the first hydrido tantalabenzocyclopent-2-ene complex reported until now, except for the telluro-formaldehyde complex [TaCp*$_2$(η^2-$TeCH_2$)H],[27] where a Ta−Te bond is described. The distances Ta−C31 [2.309(8) Å] and Ta−C38 [2.306(8) Å] are in the normal range for Ta−C single bonds. All the other parameters of the ligand are normal. No similar niobium(V) hydride metallacycle has been published either.

The ^{1}H NMR spectra of complex **4** in [D_6]benzene shows 13 signals with different multiplicities and one AB system (see Exp. Sect.), whereas in the carbon spectrum only 13 signals for the $C-H_n$ and five resonances for the quaternary carbon atoms are observed. Moreover, in the 2D ^{1}H-^{13}C heteronuclear correlation spectrum the cross peak for the ^{1}H doublet at δ = 2.60, which we assign to a classical Ta−*H* hydride resonance (T_1= 0.36 s at 233 K), was not observed. The observation of four protons and five resonances for the trimethylsilylcyclopentadienyl ring in the ^{1}H and the ^{13}C{^{1}H} NMR spectra, respectively, is due to the chiral nature of the tantalum atom.

The disposition of the hydride and the assignment of the H_α and H_β proton resonances of the Cp′ ring was realized with a differential NOE experiment by irradiating the $SiMe_3$ signal: NOE = 0.6% (δ = 3.52, H_α), 0.9% (δ = 4.55, H_β), 0.3% Ta−*H* and 0.6% *ortho*-H of phenyl ring. These data are in agreement with the location of the hydride atom close to the phenyl and trimethylsilyl groups as shown in Figure 2. The hydride is coupled (^3J = 4.4 Hz) with H38a (δ = 0.95) of the α-CH_2 group, which is in an *anti*-conformation (torsion angle ≈160°), and with H25 (δ = 4.34) of the η^5-$C_5H_4SiMe_3$ ring. Furthermore, in this spectrum we could also measure the spin-spin coupling constant (^4J = 0.85 Hz) between C_α-H38b (δ = 1.35) and the more deshielded H23 (δ = 6.14) of the Cp′ ring. This value must correspond to the "W" disposition of these protons, as shown in Figure 2c.

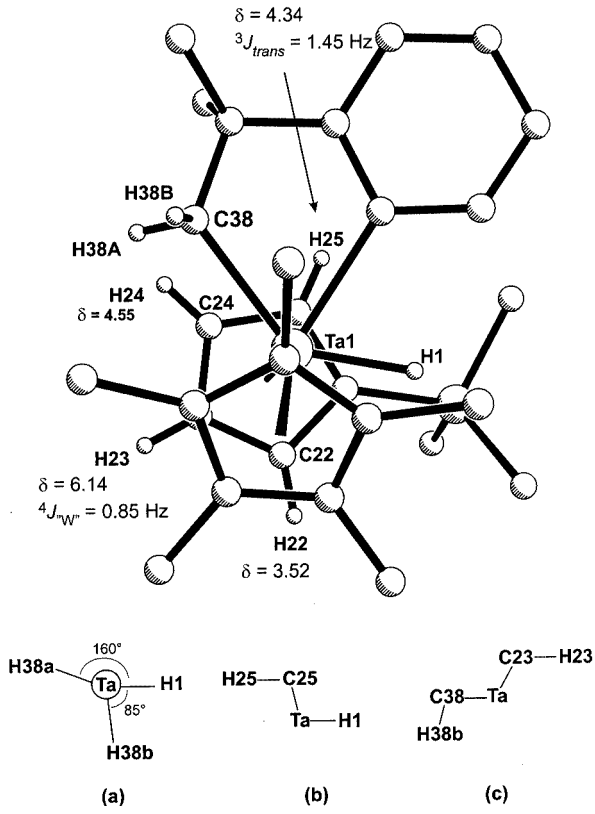


Figure 2. Top view of **4** with some relevant ^{1}H NMR spectroscopic data

Both the ^{1}H and ^{13}C spectra show a very large difference for the chemical shifts of the η^5-$C_5H_4SiMe_3$ ring (Δδ = 2.6 and 22.2 ppm, respectively) due to the cooperative electronic properties of the alkyl, phenyl and hydride groups bonded to the tantalum center.

Conclusions

The results discussed here demonstrate that μ-alkylidene tantalum and hydrido tantalabenzocyclopent-2-ene complexes can be obtained by treating the mixed dichlorodicyclopentadienyltantalum(IV) derivative [TaCp*Cp′Cl_2] with different alkylating reagents. In both cases the reaction takes place with the initial formation of dialkyl mixed tantalocene derivatives. When the alkylation is carried out with 1 equiv. of [$Mg(CH_2C_6H_5)_2(THF)_2$] or 2 equiv. of LiR (R = CH_2SiMe_3, CH_2CMe_3) the bis-μ-alkylidene complexes **1−3** are formed with simultaneous elimination of R−CH_3 (R = C_6H_5, $SiMe_3$, CMe_3). This transformation involves an α-H abstraction process to generate an intermediate tantalum(IV) alkylidene complex, which then rearranges to give a bis(μ-alkylidene) complex. However, if the starting dichloro derivative is treated with 2 equiv. of $LiCH_2CMe_2Ph$ the hydride tantalabenzocyclopent-2-ene complex **4** is isolated. Its formation can be explained by the reduction of the dialkyl derivative to give a neophyl radical, which dimerizes, and the corresponding mixed dicyclo-

pentadienyl neophyltantalum(III) derivative. A subsequent intramolecular activation of a distal aromatic C−H bond leads to **4**.

Experimental Section

General: All reactions and manipulations were carried out by using standard Schlenk techniques or in an argon-filled vacuum atmosphere glove box.[28] Solvents were refluxed over appropriate drying agents and distilled and degassed prior to use: [D_6]benzene and *n*-hexane (Na/K alloy), toluene (Na). Literature methods were employed for the syntheses of the starting materials [TaCp*Cp′Cl_2],[21] alkyllithium LiR (R = CH_2CMe_2Ph, CH_2SiMe_3, CH_2CMe_3)[29] and dibenzylmagnesium [$Mg(CH_2Ph)_2(THF)_2$].[30]

Infrared spectra were recorded with a Perkin−Elmer 583 spectrophotometer (4000−200 cm^{-1}) with samples as Nujol mulls between CsI plates or polyethylene pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Unity-300 or Varian UnityPlus-500 spectrometers; chemical shifts are referenced to the ^{13}C (δ = 128) and residual ^1H (δ = 7.15) resonances of the [D_6]benzene solvent. C and H analyses were carried out on a Perkin−Elmer 240 C microanalyzer.

Synthesis of [(TaCp*Cp′)$_2$(μ-CHR)$_2$] (R = C_6H_5, 1; $SiMe_3$, 2; CMe_3, 3) and [TaCp*Cp′(H)(η^2-CH_2−CMe_2-*o*-C_6H_4)] (4): A mixture of [TaCp*Cp′Cl_2] (0.70 g, 1.33 mmol) and [$Mg(CH_2C_6H_5)_2(THF)_2$] (0.47 g, 1.33 mmol) or $LiCH_2R$ (2.66 mmol; R = $SiMe_3$: 0.25 g; CMe_3: 0.21 g; CMe_2Ph: 0.37 g) was stirred in toluene (30 mL) at room temperature for 18 h. $MgCl_2$ or LiCl were filtered off and the resulting solution evaporated to dryness. The residue was extracted with *n*-hexane (2 × 10 mL) and cooled to −40 °C overnight to give **1**−**3** as somewhat brown (**1**) or red-brown (**2**,**3**) sticky solids and **4** as pale brown crystals.

When these experiments were carried out in a sealed NMR tube with [D_6]benzene as solvent, the elimination organic products R−CH_3 (R = C_6H_5, **1**; $SiMe_3$, **2**; CMe_3, **3**) and $PhMe_2C$−CH_2−CH_2−CMe_2Ph (**4**) were detected in the ^1H NMR spectrum.

1: Yield 0.43 g (60%). IR (Nujol): $\tilde{\nu}$ = 2950 cm^{-1} br., vs, 792 m, 1630 w, 1246 vs, 1190 w, 1169 s, 1087 s, 1025 m, 903 s, 840 br. s, 756 m, 695 m, 632 m, 479 m, 370 w. ^1H NMR (C_6D_6, 20 °C): **isomer A**, 90%, δ = 11.35 (s, *H*CC_6H_5), 7.10 (br. m), 7.05 (br. m, H_5C_6CH), 5.77 (m, 1 H), 5.04 (m, 1 H), 4.50 (m, 1 H), 4.10 (m, 1 H, $H_4C_5SiMe_3$), 1.92 (s, 15 H, C_5Me_5), 0.26 (s, 9 H, $Me_3SiC_5H_4$); **isomer B**, 10%, δ = 7.25 (br. m, H_5C_6CH), 6.58 (m, 1 H), 6.20 (m, 1 H), 6.05 (m, 1 H), 5.15 (m, 1 H, $H_4C_5SiMe_3$), 1.79 (s, 15 H, C_5Me_5), 0.30 (s, 9 H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): **isomer A**, δ = 254.4 (*C*HC_6H_5), 162.2, 141.9, 127.9, 125 (C_i, C_p, C_o, C_m, C_6H_5CH), 110.8(C_i, $C_5H_4SiMe_3$), 115.8, 114.8, 106.5, 99.7 ($C_5H_4SiMe_3$), 108.2 (C_5Me_5), 12.75(C_5Me_5), 0.47($Me_3SiC_5H_4$); **isomer B**, δ = 153, 126.2 (several phenyl, C_6H_5CH), 111 (C_i, $C_5H_4SiMe_3$), 116.8, 107.3, 101.6, 98.4 ($C_5H_4SiMe_3$), 104.2 (C_5Me_5), 11.4 (C_5Me_5), −0.69 (s, $Me_3SiC_5H_4$). $C_{25}H_{34}SiTa$ (543.56): calcd. C 55.24, H 6.30; found C 55.20, H 6.35.

2: Yield 0.57 g (75%). IR (Nujol): $\tilde{\nu}$ = 2951 cm^{-1} vs, 2905 vs, 1790 w, 1487 w, 1435 m, 1377 m, 1244 vs, 1175 m, 1047 s, 1010 m, 892 vs, 835 vs, 751 m, 674 w, 629 w, 464 w, 435 w, 347 w. ^1H NMR (C_6D_6, 20 °C): **isomer A**, 68%, δ = 10.50 (s, 1 H, *H*C$SiMe_3$), 6.26 (m, 1 H), 5.83 (m, 1 H), 4.48 (m, 1 H), 4.12 (m, 1 H, $H_4C_5SiMe_3$), 1.86 (s, 15 H, C_5Me_5), 0.33 (s, 9 H, Me_3SiCH), 0.30 (s, 9 H, $Me_3SiC_5H_4$); **isomer B**, 32%, δ = 10.42 (s, 1 H, *H*C$SiMe_3$), 6.79 (m, 1 H), 6.40 (m, 1 H), 5.03 (m, 1 H), 4.31 (m, 1 H, $H_4C_5SiMe_3$), 1.72 (s, 15 H, C_5Me_5), 0.37 (s, 9 H, Me_3SiCH), 0.35 (s, 9 H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): **isomer A**, δ = 249.4 (*C*H$SiMe_3$), 111.6(C_i, $C_5H_4SiMe_3$), 109.1(C_5Me_5), 107.2, 102.9, 102.4, 99.9 ($C_5H_4SiMe_3$), 12.5 (C_5Me_5), 4.1 (Me_3SiCH), 0.35 ($Me_3SiC_5H_4$); **isomer B**, δ = 243.2 (*C*H$SiMe_3$), 114.3(C_5Me_5), 111.3 (C_i, $C_5H_4SiMe_3$), 108.2, 106, 102, 96.75 ($C_5H_4SiMe_3$), 11.9 (C_5Me_5), 3.9 (Me_3SiCH), −0.17 ($Me_3SiC_5H_4$). $C_{22}H_{38}Si_2Ta$ (539.666): calcd. C 48.96, H 7.10; found C 48.76, H 7.19.

3: Yield 0.55 g (75%). IR (Nujol): $\tilde{\nu}$ = 2951 cm^{-1} br., s, 1780 s, 1586 m, 1455 br., s, 1377 s, 1353 m, 1245 vs, 1174 m, 1051 m, 1027 m, 957 m, 912 s, 838 br., vs, 755 m, 696 m, 633 m, 434 w, 335 m. ^1H NMR (C_6D_6, 20 °C): **isomer A**, 85%, δ = 9.85 (s, 1 H, *H*CCMe_3), 6.24 (m, 1 H), 5.68 (m, 1 H), 4.42 (m, 1 H), 4.04 (m, 1 H, $H_4C_5SiMe_3$), 1.92 (s, 15 H, C_5Me_5), 1.30 (s, 9 H, Me_3CCH), 0.29 (s, 9 H, $Me_3SiC_5H_4$); **isomer B**, 15%, δ = 10.22 (s, 1 H, *H*CCMe_3), 6.51 (m, 1 H), 5.36 (m, 1 H), 4.92 (m, 1 H), 4.68 (m, 1 H, $H_4C_5SiMe_3$), 1.62 (s, 15 H, C_5Me_5), 1.12 (s, 9 H, Me_3CCH), 0.23 (s, 9 H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): **isomer A**, δ = 249.6 (*C*HCMe_3), 111.5 (C_i, $C_5H_4SiMe_3$), 113.7, 110, 105.6, 98.5 ($C_5H_4SiMe_3$), 108.2(C_5Me_5), 49.1(Me_3*C*CH), 34.8(Me_3CCH), 13.1(C_5Me_5), 0.67($Me_3SiC_5H_4$); **isomer B**, δ = 243.8 (H*C*CMe_3), 111 (C_i, $C_5H_4SiMe_3$), 111.4, 102, 100.2, 93.9 ($C_5H_4SiMe_3$), 110.5 (C_5Me_5), 47.8 (Me_3*C*CH), 34 (Me_3CCH), 12.1 (C_5Me_5), 1.8 ($Me_3SiC_5H_4$). $C_{23}H_{38}SiTa$ (523.591): calcd. C 52.76, H 7.31; found C 52.68, H 7.27.

4: Yield 0.44 g (56%). IR (Nujol): $\tilde{\nu}$ = 1942 cm^{-1} w, 1804 w, 1596 m, 1322 w, 1293 w, 1243 vs, 1201 m, 1168 vs, 1081 m, 1063 m, 1046 m, 1030 vs, 953 w, 910 m, 870 vs, 839 vs, 814 s, 765 vs, 732 m, 702 s, 655 w, 633 m, 557 m, 430 m. ^1H NMR (C_6D_6, 20 °C): δ = 8.43, 7.25, 7.17, 7.10 (ABCD spin system, H1−H4, H_4C_6-*o*-CMe_2-CH_2-Ta), 6.14, 4.55, 4.33, 3.52 (ABCD spin system, $H_4C_5SiMe_3$), 2.60, 1.33, 0.95 (ABC, $^2J_{B-C}$ = 12.1, $^3J_{A-C}$ = 4.4 Hz, *H*-Ta-CH_2-CMe_2-*o*-C_6H_4), 1.63 (s, 3 H), 1.12 (s, 3 H, H_4C_6-*o*-CMe_2-CH_2-Ta), 1.55 (s, 15 H, C_5Me_5), 0.22 (s, 9 H, $Me_3SiC_5H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ = 155.1, 129.46, 127.76, 127.68, 125.06 (H_4C_6-*o*-CMe_2-CH_2-Ta, C_{ipso}-Ta not was detected), 116.7, 104.3, 99.4, 94.5 ($C_5H_4SiMe_3$), 107.2 (C_5Me_5), 107.1 (C_i, $C_5H_4SiMe_3$), 93.4 (H_4C_6-*o*-CMe_2-*C*H_2-Ta), 50 (H_4C_6-*o*-*C*Me_2-CH_2-Ta), 37.3, 34.4 (H_4C_6-*o*-CMe_2-CH_2-Ta), 11.53(C_5Me_5), 0.83($Me_3SiC_5H_4$). $C_{28}H_{41}SiTa$ (586.671): calcd. C 57.32, H 7.04; found C 57.28, H 6.96.

X-ray Structure Determination of 4: Crystals of compound **4** were obtained by crystallization from hexane. A suitably sized crystal sealed in a Lindemann tube was mounted on an Enraf−Nonius CAD 4 automatic four-circle diffractometer equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystallographic and experimental details of the structure are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved, using the WINGX package,[31a] by direct methods (SHELXS-97)[31b] and refined by least-squares against F^2 (SHELXL-97).[31b] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the carbon atoms to which they are attached, except for the hydride atom, which was found with the XHYDEX[31c] program, included and refined isotropically in the last cycles of refinement.

Table 2. Crystal data and structure refinement for **4**

Empirical formula	$C_{28}H_{41}SiTa$
Formula mass	586.65
Crystal habit	prismatic
Colour	pale brown
Crystal size	0.22 × 0.28 × 0.30 mm
Space group	monoclinic, $P2_1/c$
a (Å)	8.976(1)
b (Å)	16.596(1)
c (Å)	17.929(1)
β (°)	99.26(1)
V (Å^3)	2636.0(4)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.478
F(000)	1184
μ (cm^{-1})	42.27
Scan mode	ω/2θ $2.30 < \theta < 24.98$
Number of reflections	
Measured	4628
Observed	3326 ($I < 2\sigma(I)$)
Range of *hkl*	$-10 < h < 10$, $0 < k < 19$, $0 < l < 21$
Standard reflections	3 every 200 reflections
Refinement method	full-matrix least-squares on F^2
Final R indices all data[a]	$R1 = 0.0481$, $wR2 = 0.1330$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0699$, $wR2 = 0.1510$
Largest diff.peak and hole (e/Å^3)	1.929 and −2.990
Goodness of fit on F^2	1.108

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[\omega((F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$.

CCDC-174670 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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